

**The Crystal Structure of "Trichlorophenolchlorine" and
some Analogous Compounds with the Common Constitution
2,4,4,6-Tetrahalogeno-cyclohexa-2,5-diene-1-one**

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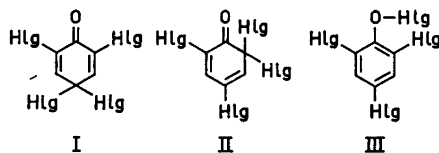
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The general formula comprises 9 compounds in which the halogen atoms are chlorine and/or bromine. They crystallize isotypically in the space group $Aba2$, unit cell dimensions are $a = 17.3-18.1 \text{ \AA}$, $b = 13.9-14.5 \text{ \AA}$, $c = 7.1-7.2 \text{ \AA}$, $Z = 8$.

The structure of the tetrachloro-compound has been determined from visually estimated X-ray data by Patterson and Fourier methods and refined by least squares techniques to the final R -value 0.13 for 704 observed reflections. The structure of the 2,6-dibromo-4,4-dichloro-compound was determined in a similar way but with less accuracy. The final R -value was 0.19 for 511 observed reflections.

The bond lengths and the surroundings of the two chlorine atoms attached to C 4 were in neither of the structures completely equivalent. The variations suggest the presence of O...Halogen-C charge transfer bonds and they may reflect the oxidative character of these substances.

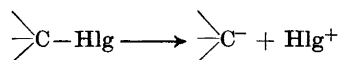
The structure of trichlorophenolchlorine (2,4,4,6-tetrachloro-cyclohexa-2,5-diene-1-one), which was first prepared 1883 by Benedikt,¹ and that of several related compounds have been subject to much discussion. Three formula types were proposed, (I-III), but in 1959 Fort² showed conclusively by



UV-, IR- and Raman-spectroscopical studies of a large number of these compounds, that the quinonoid structures (I and II) were correct. In no case did he find a structure of type III. The *ortho*-quinonoid compounds (II) are generally liquids at room temperature, and they are much less stable than the

para-quinonoid isomers (I) to which they have a tendency to rearrange. The tetrachloro compounds are much more stable than the tetrabromo analogues, and stabilities between these extremes are exhibited by structurally analogous compounds containing both chlorine and bromine.

These compounds are oxidizing agents of a rare type which act through the fission of a carbon-halogen bond, either homolytically or heterolytically as expressed by the formal process



Though Fort² had unequivocally established their chemical constitution no information was available on the molecular dimensions and we thought it worth while to try to obtain such data.

The present paper deals with a detailed X-ray structure determination of trichlorophenolchlorine and a much more crude determination of the 2,6-dibromo-4,4-dichloro analogue. The first compound was selected among the analogous substances because a pretty accurate result of the structure determination could probably be obtained and also because it is relatively stable. The second compound was used as an auxiliary for solving the first structure. Preceding the structure determination a preliminary study was made of all the related compounds in which the halogen atoms are chlorine and/or bromine. The crystallographic data obtained are summarized in Table 1. These substances all crystallize isotypically, and the morphology and elementary dimensions found agree well with the classical crystallographic investigations of trichlorophenolchlorine by Ditscheiner¹ and of tribromophenolbromine by Lewis.³

Table 1. 2,4,4,6-Tetrahalogeno-cyclohexa-2,5-diene-1-one. Crystallographic data for the isomorphous Cl and/or Br analogues. Space group *Ab*a2, *Z* = 8.

2,4,4,6-Tetrahalogenocyclohexa-2,5-diene-1-one	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Measured density
2,4,4,6-Tetrachloro-(trichlorophenolchlorine)	17.29	13.85	7.05	1.85
2,4,6-Trichloro-4-bromo-(trichlorophenolbromine)	17.4	14.2	7.1	2.06
2,4,4-Trichloro-6-bromo-	17.7	14.2	7.1	2.19 ^a
4,4-Dichloro-2,6-dibromo-	17.95	14.18	7.22	2.36
2,4-Dichloro-4,6-dibromo-	17.8	14.3	7.2	2.32
2,6-Dichloro-4,4-dibromo-	17.7	14.5	7.2	2.34
4-Chloro-2,4,6-tribromo-(tribromophenolchlorine)	18.1	14.2	7.2	2.63
6-Chloro-2,4,4-tribromo-	17.7	14.4	7.2	2.50 ^a
2,4,4,6-Tetrabromo-(tribromophenolbromine)	18.0	14.5	7.2	2.85

^a These density data are less accurate than the other.

EXPERIMENTAL

The compounds in Table 1 were prepared by reacting a 2,4,6-trihalogenophenol dissolved in 90 % acetic acid at 0°C with chlorine or bromine. The reaction product was precipitated by dilution with water and was recrystallized from tetrachloromethane.

The space group and unit cell dimensions were determined from Weissenberg photographs $hk0$ and $hk1$ and oscillation photographs with the c -axis as oscillation axis.

The structure determinations were based on intensities obtained by Weissenberg multiple film techniques using $\text{CuK}\alpha$ radiation. The intensities were estimated visually by comparison with calibrated scales, and subsequently corrected for Lorentz- and polarization effects and brought to a common level in the usual way.

From trichlorophenolchlorine 704 independent reflections were recorded using crystal fragments with approximately cylindrical cross sections. $hk0-hk6$ were recorded from a crystal of dimensions $0.24 \times 0.24 \times 0.5 \text{ mm}^3$, $h0l-h3l$ from a crystal $0.10 \times 0.10 \times 0.3 \text{ mm}^3$ and $0kl-8kl$ from a crystal $0.18 \times 0.16 \times 0.26 \text{ mm}^3$. The absorption coefficient $\mu_{\text{CuK}\alpha} = 124 \text{ cm}^{-1}$. No corrections for absorption were applied.

From 2,6-dibromo-4,4-dichloro-cyclohexa-2,5-diene-1-one 511 independent reflections were recorded from three crystal fragments of approximately circular cross sections. $hk0-hk4$ were recorded from a crystal of dimensions $0.10 \times 0.10 \times 0.4 \text{ mm}^3$, $h0l-h1l$ from a crystal $0.16 \times 0.16 \times 0.7 \text{ mm}^3$ and $0kl$ from a crystal $0.1 \times 0.1 \times 0.5 \text{ mm}^3$. The absorption coefficient $\mu_{\text{CuK}\alpha} = 177 \text{ cm}^{-1}$. No absorption correction was applied, but spot-shape corrections were made according to Phillips.⁴

STRUCTURE DETERMINATIONS

2,6-Dibromo-4,4-dichloro-cyclohexa-2,5-diene-1-one. Approximate coordinates for the halogen atoms were found from the Patterson projections $P(xy)$, $P(xz)$ and $P(yz)$. It was obvious, that the ring plane was approximately parallel to the c -plane. The trial structure was refined first by successive Fourier calculations of the centrosymmetrical projection on the c -plane, followed by a refinement of that projection by the method of Bhuiya and Stanley⁵ using an ALGOL-program by Danielsen.⁶ All z -coordinates were chosen arbitrarily to zero, except the z -coordinates for the two chlorine atoms attached to C 4 which from considerations of the bond length and the probable valency angle were fixed at ± 0.206 . At this stage of the refinement with thermal parameters applied individually and isotropically to the atoms the R -value for all observed reflections was 0.21. The final refinement of positional and anisotropic thermal parameters was made by the least squares method using the program ORFLS written by Levy, Busing and Martin.⁷ The calculations were carried out on the IBM 7090 computer at NEUCC. Final R -values and positional and thermal parameters are given in Tables 2 and 3. It should be pointed out, that the standard deviations of the positional parameters of the carbon and oxygen atoms are large (up to 0.065 Å on a coordinate) and therefore no calculations of bond lengths will be given.

Trichlorophenolchlorine. The refinement was started from a set of coordinates taken from the 2,6-dibromo-4,4-dichloro analogue. First 3 cycles of diagonal approximation least squares calculations were performed on the GIER-computer refining positional parameters and individual isotropic temperature factors. The R -value dropped from 0.21 to 0.18. At this stage 6 strong, low angle reflections were taken out of the calculations, and 3 cycles of least squares, anisotropic refinement using the program ORFLS made the R -value drop to a final value of 0.12 for the observed data. The two hydrogens in the

Table 2. Final R -values and positional parameters. The standard deviations in parentheses are multiplied by 10^4 .

Trichlorophenolchlorine				2,6-Dibromo-4,4-dichlorocyclohexa-2,5-diene-1-one.			
R -value (704 refl.) 0.13				R -value (511 refl.) 0.19			
R -value (698 refl.) 0.12				R -value (503 refl.) 0.17			
Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Cl 1	0.0211(2)	0.3278(2)	-0.021(0)	Br 1	0.0160(3)	0.3254(3)	0.000(0)
Cl 2	0.3256(2)	0.2343(2)	-0.004(20)	Br 2	0.3244(2)	0.2373(4)	0.012(20)
Cl 3	0.1181(5)	-0.0036(5)	0.197(20)	Cl 1	0.1209(8)	-0.0156(6)	0.185(30)
Cl 4	0.1163(5)	-0.0031(6)	-0.211(20)	Cl 2	0.1147(6)	-0.0005(6)	-0.209(30)
O	0.1879(5)	0.3597(6)	-0.007(30)	O	0.185(10)	0.353(10)	-0.009(50)
C 1	0.1711(7)	0.2754(9)	-0.018(40)	C 1	0.164(30)	0.274(20)	0.030(80)
C 2	0.0902(5)	0.2401(6)	0.000(40)	C 2	0.097(20)	0.240(30)	-0.019(90)
C 3	0.0724(7)	0.1460(8)	-0.017(30)	C 3	0.069(10)	0.148(20)	0.029(60)
C 4	0.1319(6)	0.0716(7)	-0.017(30)	C 4	0.134(20)	0.071(20)	-0.022(90)
C 5	0.2144(7)	0.1027(7)	-0.011(40)	C 5	0.210(20)	0.106(20)	-0.001(80)
C 6	0.2309(6)	0.1964(7)	-0.011(30)	C 6	0.226(20)	0.193(20)	0.020(70)

Table 3. Anisotropic thermal parameters $U_{ij}(\times 10^2)$ (\AA^2).

Trichlorophenolchlorine							2,6-Dibromo-4,4-dichlorocyclohexa-2,5-diene-1-one						
U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	
Cl 1	3.6	4.4	7.7	1.0	-0.6	0.7	Br 1	5.4	5.4	11.	1.1	3.1	-1.2
Cl 2	3.1	6.3	5.5	-1.1	0.1	0.7	Br 2	4.4	7.9	8.5	-1.4	0.3	-2.2
Cl 3	7.3	3.8	6.1	-0.2	1.1	2.0	Cl 1	4.5	1.9	0.6	0.0	0.6	-0.1
Cl 4	5.7	4.5	6.1	-1.5	0.8	-1.8	Cl 2	3.8	1.2	2.3	-0.3	2.6	0.1

molecule were not included in the computations. The thermal parameters of C 2 and C 4 were found to be *non positive definite*, indicating probably that the structure factors are not good enough to give reliable thermal parameters. The parameters found are given in Tables 2 and 3. Tables of the structure factors are available on request from the authors. Please refer to project number C 1052.

DESCRIPTION AND DISCUSSION OF THE STRUCTURES

Table 2 shows, that the two compounds are isostructural. Since the structure determination of trichlorophenolchlorine is much more accurate than that of the dibromodichloro-analogue, reference to the latter will in the following discussion only be made in a few cases, where deviations between the structures appear to be significant.

The structure of trichlorophenolchlorine is shown in Figs. 1 and 2, bond lengths and intermolecular distances less than 4 Å are given in Table 4, and valency angles and other angles of structural interest are listed in Table 5.

Bond lengths. The C—C bond lengths are slightly but not significantly different, and they as well as the C=C and C=O bond lengths agree well with those of equivalent bonds found in quinones, *e.g.* benzoquinone⁸ and chloranil.⁹ The C—Cl bonds in the ring plane are of the same length 1.72 Å, as found in chloranil⁹ and in various chlorine substituted aromatic rings. The bonds from the tetrahedrally surrounded C 4 atom to Cl 3 and Cl 4 are situated in a plane approximately perpendicular to the ring plane and were measured as 1.757 and 1.823 Å, respectively. The first is a normal length for this bond type, the second is unusually long. From the standard deviations on each of these measurements the statistical probability that the measured distances are different was calculated to 96 %. This means, that the two bond lengths should be regarded as “possibly different”. In the 2,6-dibromo-4,4-dichloro analogue a very large deviation was found between the corresponding C—Cl bonds, (1.62 and 2.05 Å, respectively, with standard deviations about 0.06 Å) and this difference is definitely statistically significant. Still it is not crystallographically absolutely unquestionable since systematic errors in the F_{obs} values owing to a certain decomposition of the crystals during X-ray exposures can not be completely excluded. The stretching observed in both cases of one of the C 4—Cl bonds is paralleled by a difference between the two C—Br bonds in 10,10-dibromo-anthrone. This structure has also been determined

Table 4. Interatomic distances (Å). Trichlorophenolchlorine.

<i>Intramolecular distances</i>		<i>Intermolecular distances</i> (see Fig. 1)	
Cl 1—C 2	1.720(10)	Cl 2 A—C 1 B	3.671(29)
Cl 2—C 6	1.716(11)	Cl 2 B—C 1 A	3.472(29)
Cl 3—C 4	1.823(23)	Cl 2 A—C 2 B	3.794(27)
Cl 4—C 4	1.757(22)	Cl 2 B—C 2 A	3.837(27)
O —C 1	1.205(15)	Cl 2 A—C 6 B	3.744(25)
C 1—C 2	1.479(16)	Cl 2 B—C 6 A	3.645(25)
C 2—C 3	1.344(15)	Cl 2 A—Cl 1 E	3.492(4)
C 3—C 4	1.456(16)	C 5 A—C 5 B	3.734(50)
C 4—C 5	1.499(16)	C 6 A—C 6 B	3.587(50)
C 5—C 6	1.335(14)	Cl 3 B—Cl 1 D	3.495(12)
C 6—C 1	1.497(16)	Cl 1 C—Cl 4 A	3.602(12)
Cl 3—Cl 4	2.881(16)	Cl 3 B—O D	3.078(20)
		Cl 4 A—O C	3.099(20)

Standard deviations (Å) multiplied by 10^3 are given in parentheses.

by X-ray analysis and has been refined by least squares calculations, but isotropical, individual thermal parameters were used and only a short note giving the atomic coordinates has been published.¹⁰ Though the difference between the two bond lengths (1.98 and 2.03 Å) even in this case is statistically insignificant, the combined evidence of the three structure determinations indicate, that some difference really does exist. The bond stretching may be a structural expression for the tendency to fission of a C-halogen bond which these compounds exhibit. If this supposition is correct one would in the tetrahalogenocyclohexadienones expect to find the most pronounced stretching of a C 4—halogen bond in the most unstable molecules. Since trichlorophenol-chlorine is the most stable of the compounds treated in this paper, it is not surprising, that only a small effect is found in that structure.

Valency angles and molecular packing. The valency angles deviate in some cases appreciably from the expected 120°, but this is probably connected with the very compact arrangement of the molecules in the crystal lattice. The same holds true for the small but significant deviations from planarity which has been found by comparison with a "best plane" calculated according to Schomaker *et al.*¹¹ through the nine approximately coplanar atoms, see Fig. 1. The equation of this plane (in Å) is

$$-0.0154 x - 0.0066 y + 0.9999 z + 0.1454 = 0$$

Close intermolecular contacts, about 0.1 Å shorter than the sum of the van der Waals' radii in question are found between the oxygen atom in one molecule and two C 4—bonded chlorine atoms in two adjacent molecules. These contacts link the molecules together into sheets parallel to the *a*-plane. Two such sheets, that are related by the *b*-glideplane are squeezed into the cavities of each other. The closest intermolecular contact in this double layer is of the van der Waals' type. The structure is built up of such double-layers, that are oppositely oriented and are connected in the *a*-direction by chains formed by contacts between Cl 1 and Cl 2 in adjacent molecules. This type

Table 5. Valency angles and some intermolecular angles (°). Trichlorophenolchlorine.

<i>Intramolecular angles</i>				
O	—C 1—C 2	123.8(11)	C 3—C 4—C 5	117.8(9)
O	—C 1—C 6	120.3(10)	C 4—C 5—C 6	119.1(9)
C 2	—C 1—C 6	114.1(9)	Cl 2—C 6—C 1	117.0(7)
Cl 1	—C 2—C 1	113.9(7)	Cl 2—C 6—C 5	119.1(8)
Cl 1	—C 2—C 3	121.3(8)	C 1—C 6—C 5	123.9(10)
C 1	—C 2—C 3	122.0(10)		
C 2	—C 3—C 4	121.6(10)		
Cl 3	—C 4—Cl 4	107.2(6)		
Cl 3	—C 4—C 3	107.7(12)		
Cl 3	—C 4—C 5	107.1(13)		
Cl 4	—C 4—C 3	108.0(12)		
Cl 4	—C 4—C 5	108.6(13)		
			<i>Intermolecular angles</i>	
			(see Fig. 2)	
			C 4 A—Cl 3 A...O	C 148.8(6)
			Cl 3 A...O	C—C 1 C 116.4(13)
			Cl 3 B...O	D...Cl 4 B 84.9(3)
			C 1 C—O	C...Cl 4 A 122.7(11)
			C 4 A—Cl 4 A...O	C 146.3(6)

Standard deviations (°) multiplied by 10 are given in parentheses.

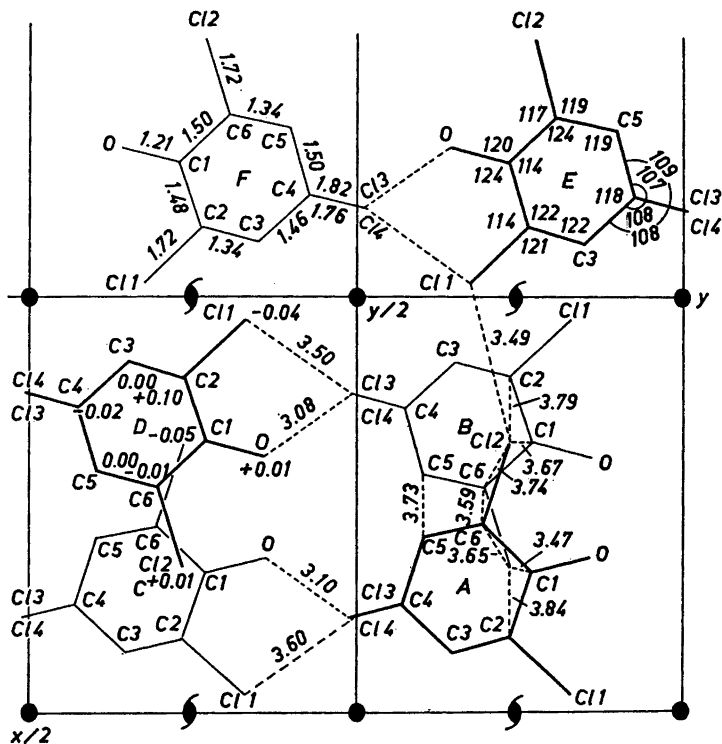


Fig. 1. Trichlorophenolchlorine, viewed along the *c*-axis. Broken lines indicate *inter*-molecular contacts.

$$A: \frac{1}{2}-x, \frac{1}{2}+y, z$$

$$C: \frac{1}{2}-x, y, z-\frac{1}{2}$$

$$E: -x, 1-y, z$$

$$B: x, \frac{1}{2}+y, z-\frac{1}{2}$$

$$D: x, y, z$$

$$F: -x, \frac{1}{2}-y, z-\frac{1}{2}$$

On the molecule *D* are indicated the distances (in Å) to a best plane through the approximately coplanar atoms.

of contact is about 0.1 Å shorter than twice the v.d.W. radius, but the corresponding repulsion between the molecules is counterbalanced by compression of the valency angles in the chain of atoms Cl 1—C 2—C 1—C 6—Cl 2. The corresponding Br—Br contact in the 2,6-dibromo-4,4-dichloro-analogue is 3.55 Å, *i.e.* 0.35 Å shorter than twice the v.d.W. radius.

Charge transfer bonds. The short intermolecular distance mentioned above between oxygen and Cl 3 (3.08 Å) together with the unusually long C 4—Cl 3 bond suggest some attraction between the molecules. This may perhaps be interpreted as a weak charge transfer bond, though the angular arrangement around the chlorine atom is unusual. The angle C—Cl...O is 149° whereas approximately collinear arrangements are generally found at the acceptor atom.¹² The idea is supported by the fact, that a charge transfer bond is

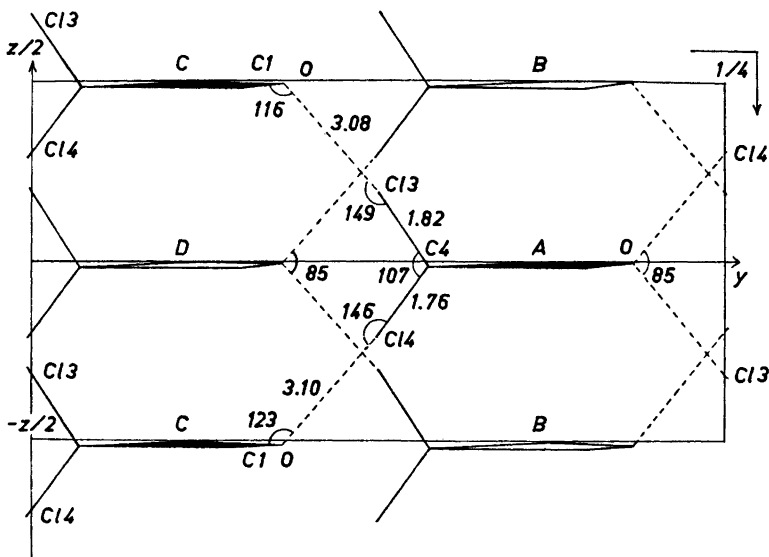


Fig. 2. Trichlorophenolchlorine, viewed along the a -axis. Broken lines indicate short intermolecular Cl...O=C distances.

undoubtedly present in 10,10-dibromoanthrone.¹⁰ In this crystal structure one of the bromine atoms — and the one with the longest C—Br bond — is situated only 2.97 Å from the oxygen in a neighbour molecule, and the atoms C—Br...O are practically collinear. In this case however, the angle C—O...Br is 146° in comparison with 116° found for the angle C—O...Cl in trichlorophenolchlorine.

Conclusions. From the structure determinations discussed above it may be concluded, that charge transfer bonds O...Halogen—C should generally be expected in crystals of quinonoid molecules containing *gem* Cl or Br atoms. Large angular deviations from the normal linear arrangement around the acceptor atom and from the normal direction towards the halogen atom of a lone pair of the oxygen atom can be anticipated because of the influence of molecular packing. Furthermore in isomerides the less stable compound should exhibit the greatest stretching of the C—halogen bond involved in charge transfer bond formation. Interesting supplementary information on the structure of this type of compounds may be obtained from low temperature X-ray structure determinations of the *ortho*-quinonoid tetrahalogenocyclohexadienones.

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